

## Room temperature $^{57}\text{Fe}$ Mössbauer characteristics of chromites from the Nuggihalli schist belt, Dharwar craton, southern India

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**Chromite samples showing ferritchromitization from the greenstone belt of south India were characterized using electron probe microanalysis and Mössbauer spectroscopy. Mössbauer study shows oxidized nature of the samples and depicts three symmetric doublets for iron, two of which are assigned to  $\text{Fe}^{2+}$ (A) and the third assigned to  $\text{Fe}^{3+}$ . Samples do not show any significant change in their equilibration temperature, which they attained during igneous cooling, in the later low-grade metamorphism undergone by the greenstone belt.**

CHROMIAN spinel commonly occurs as an accessory mineral in many mafic-ultramafic igneous and metamorphic rocks originating from the lower crust and upper mantle. Spinel has the general formula  $AB_2O_4$ , where *A* refers to a divalent metal ion (e.g.  $\text{Fe}^{2+}$ , Mg, Mn, etc.) and *B* a trivalent ion (e.g.  $\text{Fe}^{3+}$ , Al, Cr). It occurs in two types: (i) normal, where divalent cations occupy tetrahedral (*A*) sites and trivalent cations occupy octahedral (*B*) sites and (ii) inverse, where trivalent cations occur in tetrahedral (*A*) sites and octahedral (*B*) sites are occupied by both divalent and trivalent cations.

Chromite is not only a useful indicator of the crystallization environment, but it also records modifications induced during early hydrous alteration and subsequent prograde metamorphism of host rocks. Chromite first becomes rimmed and is gradually replaced by chromian magnetite or 'ferritchromite', and successively its core composition becomes modified during prograde metamorphism as a result of chemical changes with the surrounding silicates. In general, during metamorphic processes, there is  $\text{Mg-Fe}^{2+}$  substitution followed by  $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$  transformation. This implies a progressive oxidation state in the chromites. The oxidation state in spinels has been investigated by means of single-crystal X-ray refinement technique<sup>1-4</sup> and Mössbauer spectroscopy<sup>5-7</sup>. In the present study, electron probe microanalysis (EPMA) and  $^{57}\text{Fe}$  Mössbauer spectroscopy (MS) were used to obtain information on cation distribution and the oxidation state of some chromite samples from a component of the greenstone belt of south India, with the aim of providing information on their thermal history.

The chromite-bearing Nuggihalli schist belt is a linear and narrow band of metamorphosed ultramafic suite in the Archeans of Dharwar craton and is part of the primordial crust of the earth. The ultramafic rocks are altered primarily to serpentinite and talc-chlorite-tremolite schists. The major rock types of the area are peridotite/serpentinite, amphibolite, metasediments (fuchsite-quartzite, quartz-mica-chlorite and staurolite-quartz-mica schists), tonalite-trondhjemitic-gneiss (TTG) and anorthosite. The area has been subjected to greenschist to amphibolite facies metamorphism. Chromite bodies commonly occur as layers (*T* sample), high angle bands (*BY*) and in tabular or lensoid (*J*) forms. Spectacular rosy moss-like aggregates of pink chlorite occur as fracture fillings and as pockets in grey chromite ore bodies. The colours of these aggregates range from pale to rose pink. Cr-clinocllore occurs dominantly as fracture fillings and coatings around chromite grains<sup>8</sup>. Samples *BY*, *T* and *J* were collected respectively, from band, layer and tabular forms of chromites. All studied samples were ferritchromitized.

Chromite grains from sieved samples (60–80 mesh size) were separated by hand-picking. The separated samples were pulverized to about 100 mesh and then cleaned in running water. The remaining silicate minerals were picked up and the chromite samples were repeatedly passed through a Frantz isodynamic separator. The samples were then treated with clerici solution. The separated samples were finely pulverized (~350 mesh) in agate mortar and grounded till homogeneity of grain size ensued. The powdered samples were used for Mössbauer study. The samples were polished by Buehler Automat (model no. 850) and other polishing auxiliaries for the chemical study.

The chromite samples were chemically analysed by a JEOL-733 superprobe microanalyser with wavelength dispersive method at 15 kV, with a beam current of 0.01  $\mu\text{A}$  and beam diameter of 10  $\mu\text{m}$ . Average spectrum counts (10 s  $\times$  5 times) were compared with standards of natural minerals and data were reduced by Bence and Albee method<sup>9</sup>. Chemical compositions presented in Table 1 are averages of five spot analyses made in individual samples. Each element determination was accepted after checking that measurements of standards before and after sample determination were within  $\pm 1\%$ . Total iron is recalculated to  $\text{FeO}$  and  $\text{Fe}_2\text{O}_3$  based on the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ratios obtained from the Mössbauer study. Cations are calculated on four oxygen basis.

Room temperature (298 K) Mössbauer spectrum was recorded in a Wissenschaftliche-make conventional constant acceleration drive with a  $^{57}\text{Co}$  (in Rh matrix) source of ~10 mCi at Saha Institute of Nuclear Physics, Kolkata. Based on the iron content (known from EPMA results, Table 1), the finely powdered samples were spread uniformly over an area of 2  $\text{cm}^2$ , making the absorber thickness ~10  $\text{mg}/\text{cm}^2$  to optimize thickness effect. The spectrum was recorded in transmission using a 512-channel analyser in timescale mode. The spectrometer was

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calibrated against a high purity (99.99%) natural iron foil of 25  $\mu\text{m}$  thickness (supplied by Amersham International PLC). The spectra were fitted with Lorentzian lines with a nonlinear least squares fit program of Meerwall<sup>10</sup>. For each doublet the intensity and line width were constrained to be equal. The precision in the distribution data is estimated to be  $\pm 2\%$ .

Interpretation of Mössbauer spectra of chromite is difficult because of strong peak overlaps. Assuming no difference in recoil-free fractions ( $f$ ) between sites in spinels<sup>11</sup>, the peak areas of the doublets are assumed to correspond directly to the quantitative occupancies<sup>6</sup>.

**Table 1.** Cation distribution of chromite using electron microprobe analysis and Mössbauer spectroscopy

	<i>BY</i>	<i>T</i>	<i>J</i>
MgO	8.95	8.36	3.97
Al <sub>2</sub> O <sub>3</sub>	6.49	6.85	7.48
SiO <sub>2</sub>	0.02	0.07	0.00
TiO <sub>2</sub>	0.54	0.59	0.67
Cr <sub>2</sub> O <sub>3</sub>	56.94	56.32	55.33
MnO	0.41	0.43	0.47
FeO	13.66	14.32	17.43
Fe <sub>2</sub> O <sub>3</sub>	11.18	12.70	16.08
NiO	0.06	0.10	0.07
CaO	0.01	0.00	0.03
Na <sub>2</sub> O	0.00	0.02	0.03
Sum	98.24	99.76	101.56
<i>A site</i>			
Mg	0.453	0.430	0.209
Al	0.000	0.000	0.000
Si	0.001	0.001	0.000
Mn	0.011	0.012	0.012
Fe <sup>2+</sup>	0.235	0.216	0.247
Fe <sup>3+</sup>	0.297	0.330	0.417
Ni	0.002	0.003	0.002
<i>B site</i>			
Mg	0.000	0.000	0.000
Al	0.271	0.270	0.301
Ti	0.014	0.016	0.016
Cr	1.544	1.515	1.511
Fe <sup>2+</sup>	0.165	0.187	0.276
Fe <sup>3+</sup>	0.000	0.000	0.000

However, a difference between  $f$ 's of Fe<sup>2+</sup> and Fe<sup>3+</sup> has also been reported<sup>12</sup>. Two models are generally adopted for fitting of such spectra. In one model, distribution of Fe<sup>2+</sup>(*A*) and Fe<sup>3+</sup>(*B*) at tetrahedral and octahedral sites respectively, is presumed, as in a normal spinel<sup>13–15</sup>. This model excludes the possibility of the presence of Fe<sup>3+</sup>(*A*) or Fe<sup>2+</sup>(*B*) in chromite and did not address the problem of site occupancies of complex natural spinels forming at high temperature and/or in an oxygenated environment.

The second model, involving disorder, considers the occupancy of either Fe<sup>2+</sup> or Fe<sup>3+</sup> or both at the tetrahedral site, and works well for Cr-spinels having complex chemical composition<sup>16,17</sup> or forming in an oxidizing environment<sup>6,18</sup>. Natural chromite samples often show disorder distribution of Fe<sup>2+</sup> and Fe<sup>3+</sup> between *A* and *B* sites at high temperature<sup>19–21</sup>. Our samples contain appreciable amounts of Mg, Al, Fe and underwent a complex thermal history; therefore, a partial disordered nature is possible.

The room-temperature spectra recorded in this study were fitted using both the models. The second model fit showed better  $\chi^2$  and hyperfine parameters, and is considered in this work (Table 2).

All the samples (*BY*, *T* and *J*) show Mössbauer spectra where three main peaks (marked I, II, III in Figure 1) could be visually identified. The spectra were fitted (based on the second model), at first two doublets within the first and second peaks (I, II) of the lower velocity region. The less intense peak (III) on the higher velocity side was fitted with one wing at the least intense peak (III) and the other wing at the highest intense peak (I) of the lower velocity region, and another doublet was restricted within the peak (III) on the higher velocity side.

<sup>57</sup>Fe hyperfine parameters, distribution of Fe<sup>2+</sup> and Fe<sup>3+</sup> at the respective sites, Fe<sup>3+</sup>/Fe<sup>2+</sup> ratios and  $\chi^2$  of the fitting are listed in Table 2. Results are expressed in terms of isomer shift (IS), quadrupole splitting (QS), line width ( $\Gamma$ ), area of the spectrum (%) assigned to each quadrupole component and the ratio of Fe<sup>3+</sup>/Fe<sup>2+</sup>. An uncertainty of about 5% in the Fe<sup>3+</sup>/Fe<sup>2+</sup> value is calculated from our spectra. Cation distribution recalculated considering the MS results is reported in Table 1.

**Table 2.** Mössbauer hyperfine parameters and distribution of Fe<sup>2+</sup> and Fe<sup>3+</sup> at different sites of chromites and Fe<sup>3+</sup>/Fe<sup>2+</sup> ratios from the spectral areas (at 298 K)

	IS (mm/s)	QS (mm/s)	Site	Area of the doublet (%)	Line width ( $\Gamma$ ) mm/s	$\chi^2$	Fe <sup>3+</sup> /Fe <sup>2+</sup>
<i>BY</i>	0.13	0.43	Fe <sup>3+</sup> ( <i>A</i> )	44.80	0.36	1.65	0.81
	0.73	0.78	Fe <sup>2+</sup> ( <i>A</i> )	32.50	0.36		
	1.08	0.43	Fe <sup>2+</sup> ( <i>B</i> )	22.70	0.36		
<i>T</i>	0.13	0.43	Fe <sup>3+</sup> ( <i>A</i> )	46.60	0.30	1.78	0.88
	0.65	0.60	Fe <sup>2+</sup> ( <i>A</i> )	28.60	0.30		
	0.91	0.69	Fe <sup>2+</sup> ( <i>B</i> )	24.40	0.30		
<i>J</i>	0.09	0.52	Fe <sup>3+</sup> ( <i>A</i> )	48.00	0.30	1.20	0.92
	0.69	0.87	Fe <sup>2+</sup> ( <i>A</i> )	24.00	0.40		
	1.27	0.52	Fe <sup>2+</sup> ( <i>B</i> )	27.40	0.40		

$\text{Fe}^{2+}$  of a regular tetrahedral (A) site of cubic symmetry in a spinel structure would show no quadrupole splitting and should show a singlet. But the observed QS for  $\text{Fe}^{2+}$  (A) in our samples could be due to lifting of the degeneracy of low-lying crystal field states<sup>22</sup> caused by: (i) the substitutional distribution of  $\text{Cr}^{3+}$ ,  $\text{Al}^{3+}$ , etc. of different atomic radii at octahedral sites generating a strain<sup>23</sup>; (ii) an induced anisotropy of the electric field gradient (efg) at the  $\text{Fe}^{2+}$ (A) nucleus by trivalent cation substitution in the next nearest cation sphere<sup>15</sup>; and (iii) vacancy coupled with  $\text{Fe}^{3+}$  resulting from oxidation<sup>6</sup>.

At site A, the NNN effect on QS of  $\text{Fe}^{2+}$  is more evident compared to that on  $\text{Fe}^{3+}$ (A), which is spherically symmetric  $3d^5$  configuration compared to the  $3d^6$  of  $\text{Fe}^{2+}$ ; in addition, the low-lying electrons of  $e$ -orbitals of  $\text{Fe}^{3+}$  (A) are perhaps less amenable to Jahn–Teller distortion and consequently lesser degeneracy loss<sup>7</sup> compared to  $\text{Fe}^{2+}$ . In many normal spinels, the QS of  $\text{Fe}^{2+}$  at the tetrahedral site is smaller than that of  $\text{Fe}^{3+}$ . This is explained as due to random distribution of varying trivalent ions with different ionic radii over octahedral B sites<sup>24</sup>. In oxide spinels, QS of  $\text{Fe}^{3+}$  for tetrahedral or octahedral sites is small (0.3–0.6 mm/s).  $\text{Fe}^{2+}$  at these sites shows small to large QS values, depending on the disorder in near-neighbour sites. According to the existing literature, the outer part of the absorption envelope may be due to ferrous iron, in tetrahedral and/or octahedral coordination in the spinel structure<sup>25–27</sup>. A broad absorption for  $\text{Fe}^{2+}$  in tetrahedral coordination can be expected due to next-nearest (NNN) effect, i.e. non-spheric cation distribution in the second coordination sphere of this site<sup>28</sup>. Moreover, inner doublets may be determined<sup>25,27</sup> by octahedrally coordinated  $\text{Fe}^{2+}$ . However, these effects may not account for the large asymmetry displayed by the spectra of our chromite samples; hence an absorption band due to ferric iron, which contributes in the range zero to 1 mm/s, is considered.

The room temperature (298 K) Mössbauer spectra of *BY*, *T* and *J* show three sets of doublets (spectra for samples *T* and *J* are presented in Figure 1) with respective isomer shifts 0.13, 0.73, 1.08 mm/s (for sample *BY*); 0.13, 0.65, 0.91 mm/s (for sample *T*) and 0.09, 0.69, 1.27 mm/s (for sample *J*). The first doublets with IS 0.13 mm/s (sample *BY*), 0.13 mm/s (sample *T*) and 0.09 mm/s (sample *J*) were assigned to  $\text{Fe}^{3+}$ (A), in accordance with earlier reports<sup>6,7,16–18,29,30</sup>. The doublets with IS 1.08, 0.91 and 1.27 mm/s were assigned to octahedral  $\text{Fe}^{2+}$ , which is in agreement with previous workers<sup>17,18,29</sup>.

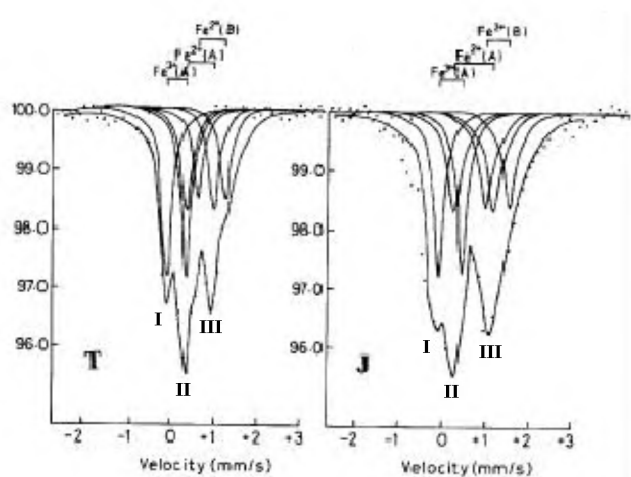
Researchers are still not unanimous over the assignment of doublets showing IS 0.61 to 0.81 mm/s. The difficulty in interpretation of these doublets is due to the choice between two contradictory assignments. Some workers interpret doublet with IS 0.67 to 0.80 mm/s as due to interelectronic exchange between  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  as common in magnetite<sup>31</sup>. Doublet with IS 0.67 to 0.76 mm/s and QS 1.36 to 1.70 mm/s are typical<sup>32</sup> of  $\text{Fe}^{2+}$ . Galvao Da Silva *et al.*<sup>17</sup> assigned doublets with IS 0.80–1.00 mm/s and QS 1.36–1.70 mm/s to  $\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+}$ (B) (electron hopping). Similar electron hopping in chromite was also reported by Fatseas *et al.*<sup>16</sup>, but with lower isomer shift values. Recently, the concept of the electron hopping in Cr-spinels has been discarded<sup>6,13,14,29</sup> and assigned to tetrahedral  $\text{Fe}^{2+}$  for the doublets with IS 0.85–0.95 mm/s<sup>13,29,30</sup> and QS ranges from 0.75 mm/s<sup>13</sup> to 2.09 mm/s<sup>30</sup>.

For Nuggihalli chromites, the three sets of doublets (Figure 1) do correspond to  $\text{Fe}^{3+}$  (A),  $\text{Fe}^{2+}$ (A) and  $\text{Fe}^{2+}$ (B) (Table 2) and occur as disordered to partial inverse spinel forms.  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ratios (Table 2) indicate that all the chromite samples are oxidized.  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ratios<sup>33</sup> for the unoxidized Archaean greenstone belt chromites range between 0.00 and 0.25. Higher  $\text{Fe}^{3+}/\text{Fe}^{2+}$  value depends on the degree of ferritchromitization in the sample. The most ferritchromitized sample *J* has a higher value (0.92) than samples *T* (0.88) and *BY* (0.81).

In summary, MS analyses demonstrate the general oxidation state of chromites from Nuggihalli schist belt, whereas single-crystal refinement study demonstrates substantially no oxidation state for the unaltered core samples<sup>4</sup>. These conflicting results are primarily due to the differences in the techniques employed. In MS analysis a powder sample is used, and large numbers of crystals involving both cores and rims of crystals get into the powder. In contrast, single crystal technique probed the selected core of crystals, which were not altered.

The intra-crystalline Mg–Al distribution between A and B sites of natural spinels mainly depends on the thermal history of the host rocks. When cooling is slow, Mg and Al cations order strongly in A and B sites respectively, whereas fast quenching preserves disordered distribution<sup>34–36</sup>. The dependence of cation distribution on temperature has been investigated by several authors<sup>19,20,34,37,38</sup>.

In the present study, the chromite–olivine assemblage calibration proposed by Fabries<sup>39</sup> was used to determine



**Figure 1.** Room temperature Mössbauer spectra of Nuggihalli chromites.

the equilibrium temperature inter-crystalline cation exchange of chromite ores. The following parameters were calculated from coexisting chromite and olivine phases in an unaltered peridotite relict (details presented elsewhere<sup>40</sup>);  $X_{Mg}^{Sp} = 0.474$ ,  $X_{Fe}^{Sp} = 0.517$ ,  $X_{Mg}^{Ol} = 0.890$ ,  $X_{Fe}^{Ol} = 0.109$ ,  $\gamma_{Cr}^{Sp} = 0.759$ ,  $\gamma_{Fe2+}^{Sp} = 0.222$ ,  $K_D = 8.868$ ,  $\ln K_D = 2.18$ ,  $\ln K_D^0 = 1.292$ . On this basis, the temperature of formation of Nuggihalli chromite has been determined<sup>40</sup> as 1178°C. This high temperature does not fit clearly with those indicated by the greenschist facies. Considering that the chromite was subjected to greenschist facies metamorphism, the indication of a relatively low equilibration temperature (e.g. 400–500°C) for the chromite crystals would be reliable. This may arise if the primary compositions are relicts of the original cooling stage, and have not substantially reset during later greenschist metamorphism or alteration<sup>41</sup>. Following Barnes<sup>41</sup>, it may be postulated that chromites in the Nuggihalli schist belt were not affected by greenschist-facies metamorphism, while the equilibrium temperature determined from cation exchange in chromite as 1178°C, corresponds to the original igneous cooling. Therefore, the low temperature indicated by high order of cation distribution is not real, but was caused by the 'buffer' effect of very high Cr contents.

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## Malaria epidemicity of Mewat region, District Gurgaon, Haryana, India: a GIS-based study

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**A GIS-based study was initiated in Mewat region, District Gurgaon, Haryana, an integral part of traditionally known malaria epidemic belt of the Northwestern Plains of India. The study included (i) delineation of malaria paradigms at macro level; (ii) identification of eco-epidemiological characteristics of each paradigm, and (iii) identification of the paradigm receptivity for malaria.**

**Using RS and GIS, the five easily recognizable malaria paradigms, namely irrigation command, catchment/non-catchment, mining, urban and flood-prone areas, were mapped. Each paradigm exhibited its own eco-epidemiological characteristics and potential for maintaining malaria transmission of varying intensity. Paradigm-wise receptivity revealed that during 1996, an epidemic year, different paradigms responded differently. Although all paradigms showed upward trend, maximum amplification occurred in urban/semi-urban paradigms. During 1993 and 1998, i.e. in the last two inter-epidemic periods, flood-prone paradigm, irrigation command area II and non-catchment area continued to retain active pockets of malaria, namely Akeri and Malab sections in Nuh block; Uleta and Kankar Kheri in Nagina block; Biwan in Ferozpur Jhirka block; Punhana, Hathana gaon, Sunhera and Tirwara in Punhana block. With the current inter-epidemic period starting from 1998 onwards, any ecological change in the scenario influencing the above three paradigms favourably, may flare up malaria cases from hot pockets. Therefore there is a need to strengthen surveillance in these areas and pay special attention to these pockets.**

Mewat region, District Gurgaon, Haryana carved out of erstwhile Punjab in November 1966 as a result of reorganization of states, is an integral part of traditionally known malaria epidemic belt of the Northwestern Plains of India. This belt is associated with unusual monsoon rains and other socio-economic factors, changing the malaria scenario at an interval of 7–9 years<sup>1–3</sup>. During the post-independence period, the Government of Haryana established the Mewat Development Authority for this region to regulate developmental and economic activities, aimed at improving irrigated and rain-fed agriculture, flood control, recharging of groundwater, provision of safe drinking water to villages and a host of other activities, viz. crop development, horticulture and livestock improvement (P. V. Ramesh *et al.*, 1999, unpublished report).

Proponents of Global Malaria Control Strategy (1993)<sup>4</sup> recognizing that the malaria problem varies enormously from epidemiological, ecological, social and operational view-points, recommended identification of easily recognizable eco-epidemiological types, namely malaria paradigms for local analysis for formulation of eco-friendly, cost-effective and sustainable control strategies. It is in this context that a GIS-based study was initiated for (i) delineation of malaria paradigms at macro level; (ii) identification of eco-epidemiological characteristics of each paradigm, and (iii) identification of the paradigm receptivity for malaria in Mewat region. The results of this study are presented in this communication.

The study area comprises of six blocks, viz. Nuh, Nagina, Taroru, Ferozpur Jhirka and Punhana in Gurgaon district and a small portion of Hatin block of Faridabad district, Haryana, which is located about 120 km south of Delhi (Figure 1). The total population of the region is 0.89 mil-

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